THE ACTIVITY COEFFICIENTS OF MIXTURES OF ELECTROLYTES. THE UNSYMMETRICAL ELECTRIC TYPE EFFECT.

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DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Sience
of Columbia University.

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BY
CHARLES F. MASON
NEW YORK CITY
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ACKNOWLEDGMENT

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THE ACTIVITY COEFFICIENTS OF MIXTURES OF ELECTROLYTES. THE UNSYMMETRICAL ELECTRIC TYPE EFFECT.

ABSTRACT OF DISSERTATION

I. What was attempted?

(1a) The determination of the activity coeffcients of salts of high and unequal valence type in the presence of solvent salts of different valence types.

(1b) To determine in what manner the peculiarities previously noted for mixtures of salts of these types called for simplicity the "unsymmetric electric type effect" would vanish with the concentration.

(1c) To investigate the range of concentration over which the Debye-Hückel theory in its present form would account for the experimental behavior of such mixtures.

II. In how far were the attempts successful?

(2a) The actual values of the activity coefficients of salts of high and unequal valence types, over a concentration range varying from 0.00008 molar to 0.10 molar have been determined.

(2b) The activity coefficients of salts in mixtures, which display the so called "unsymmetric electric type effect" have been plotted as a function of the total salt concentration.

(2c) The deviations of the actual values of the activity coefficients of salts in such mixtures, from the values calculated by the simple Debye-Hückel equation have been calculated.

III. What contibutions actually new to the science of chmeistry have been made?

(3a) It has been shown for the first time that the "unsymmetric electric type effect" does not vanish with sufficient

rapidity in highly dilute solutions (0.00008 molar) to make the rule of ionic strength a principle of general validity. Some factor of physical nature, which is not adequately accounted for by the Debye-Hückel theory in its present form, and consequently by the principle of ionic strength, is involved in the general case.

(3b) When the curves showing the relations of the deviation of the activity coefficient from the ideal limiting law of Debye and Hückel, to the first power of the Ionic Strength, are studied it is found that mixtures of symmetrical valence types differ markedly from those of unsymmetrical types.

(3c) In highly dilute solutions of a (3—1) salt dissolved in a (2—2) solvent salt, where the concentration ranges from 0.00008 molar to 0.10 molar the experimental data show a sharp positive deviation, from the limiting law of Debye and Hückel and consequently from Lewis and Randall law of ionic strength, at the lowest concentration studied, followed by a strictly linear negative deviation.

(3d) When the solvent salt is of opposite valence type from the saturating salt (ex. a (3—1) in a (1—2) type the deviations of the experimental data from the limiting law of Debye and Hückel are most marked and show a sharp positive deviation at lowest concentrations; (ex. 0.0005 to 0.01 molar) followed by a strictly linear deviation extending from 0.01 M. to the highest concentration studied 0.10 molar.

(3e) When the valence type of the solvent salt is of the same sequence as that of the saturating salt (ex. (3—1) in a (2—1) type) the deviation from the ideal law was always found to be negative and of linear character in accordance with previous theory. These deviations are discussed from the standpoint of the Debye-Hückel Theory.

(3f) Additional evidence has been obtained for the validity of the limiting law of Debye and Hückel for symmetrical solvent types and for the numerical value of the theoretical constant given by Brönsted and La Mer.

INTRODUCTION

According to the theory of complete dissociation of strong electrolytes as developed by Bjerrum, Milner and others, the deviations which salt solutions exhibit from the laws of perfect solutes as measured by their activity coefficients are to be attributed solely to their inter-ionic electrostatic forces. The most successful attempt to formulate the laws of inter-ionic attractions is contained in the elaborate work of Debye and Hückel [1] (Debye and Hückel, I., Physik. Zeit., 24, 185, 1923.) They base their theory upon the assumption of complete dissociation and three universally accepted generalizations; namely: Coulcomb's Law, Boltzman's Principle of probability distribution and Poisson's equation for the space variation of the electric potential in terms of the density of electricity. *With the aid of the fundamental physical assumption that an ion may be considered as a first approximation as a rigid non-polarizable body possessing a uniform spherical distribution of the electric charge over its surface of action,* Debye and Hückel have derived mathematical expressions by which the activity coefficient can be calculated for dilute solutions simply from a knowledge of the numbers and valence types of the salts present in a given volume of solvent and the average apparent diameter "a" of the spheres over which the ionic charges are distributed. On the whole their equations have been shown by a number of writers[2, 3, 4], to be in excellent accord with the experiemntal facts. ([2] Brönsted and La Mer, J. Am. Chem. Soc., 46, 555, (1924)). ([3] A. A. Noyes, ibid 46, 1080-1098, (1924)). ([4] Scatchard ibid, 47, 651 and 2098, (1925)).

In their attempt to explain the variation of the activity coefficient of an electrolyte when present in mixtures of electrolytes differing in valence type and concentration, Lewis and Randall. ([5] Lewis and Randall, J. Am. Chem. Soc., 43,

1112, (1921) or Thermodynamics New York, 1923, pps.373-374) formulated the important concept of the "ionic strength" of a solution as a unit for expressing the concentration in such mixtures and enunciated the general principle; namely: *that in dilute solutions of strong electrolytes the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.* However, they did not specify the numerical values of the constants involved or the exact form of the concentration law, which each type of salt should exhibit.

Brönsted and La Mer pointed out that the principle of Lewis and Randall was included in the limiting forms of the Debye-Hückel theory and proved conclusively that in the region of highly dilute solutions, the activity coefficient of a salt could be accurately accounted for by the equation.

$$\text{I.} \qquad -\text{Log}_{10} f\,(\text{salt}) = \alpha^1(-Z_1Z_2)\sqrt{\mu}$$

Here $Z.Z_2$ represent the valences of the cation and anion of the binary salt whose activity coefficient is being considered, the valence henceforth always being considered positive for the cation and negative for the anion; μ represents the ionic strength of the solution which is defined as one-half of the sum of the molar concentrations of all ions in the solution, each ion multiplied by the square of its valence, thus

$$\text{II.} \qquad \mu = \tfrac{1}{2} \sum_{1}^{s} \text{nj}Zj^2$$

nj equals the number of moles of ions of the Jth sort per liter of solution and the summation is taken over all ions from I — J —S. Lewis and Randall define the ionic strength in terms of the molal concentration (moles per 1000 gr. of water), but since the electrostatic forces must be correlated with the distance between ions, we consider it best to define μ in terms of volume concentration as Debye and Hückel have done. The difference is of no particular importance in dilute

solutions but introduces difficulties in concentrated solutions. f represents the stocihiometic activity coefficient of the salt (See foot-note, p. 328, Lewis and Randall, Thermodynamics, 1923) and a^1 is a constant the value of which is predicted from theory; it equals 0.505 at 25° C.

In Equation I. the question of ionic size is omitted; consequently it is valid only for solutions which are so dilute that it becomes permissable to consider the ions as though they were point charges. In order to account for the individual behavior of the activity coefficients in less dilute solutions Debye and Hückel introduced the assumption noted in paragraph one regarding the physical structure of the ions which they justly characterize as a "rather far reaching approximation." The effect of ionic size is expressed by Equation III

$$\text{III.} \qquad -\text{Log}_{10} f = a^1(-Z_1Z_2)\sqrt{\mu}\,\frac{1}{1+X}$$

where $X = 0.325.10^8\, a\sqrt{\mu}$, X is a dimension less variable depending upon "a" and the ionic strength. It represents the ratio between the diameter "a" and the reciprocal of the characteristic distance $1/\varkappa$ at which the potential of the ion under consideration has fallen to 1/e of its value owing to the presence of other ions. If Equation III. is expanded in terms of X we obtain

$$\text{IIIa.} \qquad -\text{Log}_{10} f = a^1(-Z_1Z_2)\sqrt{\mu} - a^1(-Z_1Z_2)\sqrt{\mu}\,\frac{X}{1+X}$$

or in terms of ascending powers of $\mu^{1/2}$ as

$$\text{IIIb.} \qquad -\text{Log}_{10} f = a^1(-Z_1Z_2)\sqrt{\mu} - 1.65\cdot 10^7\, a(-Z_1Z_2)\mu + 5.5\cdot 10^{14} a^2(-Z_1Z_2)\mu^{3/2} + \ldots$$

Equations III. a and III. b show that a positive value for the average apparent diameter of the ions should lead uniformly to smaller numerical values for $-\log_{10} f$ depending upon the value of "a" i.e., the deviations from Equation I. should be negative and in reasonably dilute solution linear in character,

with respect to the ionic strength, since the second term of Equation III. b is the predominant one in such solutions. Thus by subtracting Equation I. from III. b, or Equation I. from III. a we obtain respectively IV.a and IV. b.

$$\text{IVa.} \qquad \text{Deviation} = -\text{Log}_{10}\frac{f}{f\ (\text{ideal})} = -1.65 \cdot 10^{7}a(-Z_1Z_2)\mu + \ldots$$

$$\text{IVb.} \qquad \text{Deviation} = -a_1(-Z_1Z_2)\sqrt{\mu}\left\{\frac{X}{1+X}\right\}$$

as the equations for the deviations from the laws of ideal salt solutions on the assumption of spherical non-polarizable ions of average diameter "a." Equation III. was tested by Schärer, (Schärer, Physik Zeit., 25, 145 (1924) working in Debye's laboratory, by comparing the data available in 1923. On the whole there is an excellent agreement up to 0.30 μ in many of his calculations if we use values of "a" ranging between 1—6. 10^{-8} cm. However, we must note that it was necessary for Schärer to assume a negative value of "a" a—physical impossibility,—in order to account for the effect of KNO_3 on the solubility of Tl (NO_3); *this discrepancy cannot be ascribed simply to experimental error for there are other data usually involving nitrates and sulphates, which would require negative values of "a."* For example some data obtained by Brönsted and La-Mer[2] give suggestive evidence, that other factors are operating. New experimental data will be given in this paper showing that although the linear negative deviation of the activity coefficient seems to be the normal behavior, nevertheless there are some very marked abnormalities in mixtures of highly unsymmetrical valence types.

THE UNSYMMETRIC ELECTRIC TYPE EFFECT

Previous to Debye's investigations, Brönsted [(J.A.C.S., 44, 877, (1922), See also letter to Lewis and Randall; Thermo-

dynamics, pps. 368-9),] had rejected the principle of the ionic strength as a *complete* solution of the problem and proposed instead, the principle of specific interaction and the linear deviation of the activity coefficient (J.A.C.S., 45, 2898 (1923). (He based his objections to the ionic strength principle largely upon the experiments of Miss Peterson (Brönsted and Peterson, 43, 2265, (1921)), who found that in the case of ions of valence greater than unity; the effect of the ion of opposite sign increases with increasing valence. They stated that "in all cases the activity of a given ion depends more upon the nature of the ions of opposite sign than it does upon ions of the same sign, a point of importance in the general conception of salt solutions."

Brönsted and La Mer in accepting the ionic strength principle as a limiting law, called attention to the fact that this phenomena which we will call the unsymmetric type effect could not be accounted for by the use of the Ionic Strength Principle. They raised the question whether or not this abnormality would vanish with decreasing concentration in the same manner as does the linear deviation effect described above. (See Equation IV. a).

In view of the evidence then available they emphasized that their otherwise excellent confirmation of the Debye-Hückel theory in its present form did not extend to mixtures of highly unsymmetrical valence types as for instance a (3—1) salt like Luteo di ammino tetra nitro cobaltiate $Co(NH_3)_6[(Co(NH_3)_2(NO_2)_4)]_3$. dissolved in an aqueous solution of a (1—2) solvent salt like K_2SO_4 or a (3—1) salt like Luteo di ammino di nitro oxalo cobaltiate $Co(NH_3)_6[(Co(NH_3)_2(NO_2)_2C_2O_4)]_3$ in an aqueous solution of a (2—2) solvent salt like $MgSO_4$. This provision is equivalent to stating that the thermodynamic properties of the ions of salt mixtures of highly unsymmetrical valence type cannot be accounted for completely even in highly dilute solution on the assumption that the potential of such an ion is a function only of the number and the square of its valences as the acceptances of The Lewis and Randall principle necessitates. It accordingly be-

comes of particular interest to inquire whether the mathematical approximations and simplifications which Debye and Hückel were obliged to make in order to arrive at Equation III. will be sufficient to account for this phenomenon or whether it will be necessary to revise and extend their physical assumption of the spherical and non-polarizable character of the ideal ion.

That the first possibility might easily prove to be sufficient becomes clear when we note that in the expansion of the exponential in the right hand member of the fundamental Equation of Poisson involving the density of electricity.

$$\text{V.} \qquad \frac{d^2\phi}{dr^2} + \frac{2}{r}\frac{d\phi}{dr} = -\frac{4\pi\epsilon}{D}\sum_1^s nj\,Zj\,e^{-Zj\frac{\epsilon\phi}{kT}}$$

that Debye and Hückel neglected all terms beyond the second. The first term vanishes since $\Sigma\, njZj$ always equals zero, as the sum of the number of equivalents of positive and negative electricity must equal zero to preserve electrical neutrality for the solution as a whole. [References. Equation 21 of Debye and Hückel, Physik. Zeit. 24, 193 (1923). See also A. A. Noyes, J. A. C. S., 46, 1080 (1924), and Eucken, Jette and La Mer, Fundamentals of Physical Chemistry, loc. cit. foot-note p. 326.] It can be shown that the second or remaining terms of the expansion always involves the ionic strength $\sum_1^s njZj^2$ as the concentration factor while the succeeding neglected terms involve a concentration factor increasing in integer powers of the valence Z for each term. Thus if we retain the third term in the expansion of Equation V. we must consider the cubes of the valences of all the ions. It is easy to see that when the valences of the cations and anions are equal, the concentration factor namely $\sum_1^s njZj^3$ always vanishes but when the valences of the cations and anions are unequal, $\sum_1^s njZj^2$ may possess values of considerable magnitude depend-

ing upon the concentration and the degree of inequality in the valences. The case of symmetrical electrolytes was considered by Debye and Hückel as a careful study of their first paper will show that their equations were derived specifically for KCl. They did not mention the case of unequal valences but point out that the higher valence terms of even powers (Ex. Z^4) were quite negligible except at very high concentrations. We are indebted to Professor Debye for deriving in February, 1925, an equation involving the third term. His kindness was an inspiration for us to attempt an explanation of the data on this basis.

Unfortunately the Mathematical complexities involved in carrying to completion the calculations necessary to make an exact test of the complete expansion of Equation V., proved to be too great a task to complete at this time. We shall accordingly confine the purpose of this dissertation to investigating the unsymmetric electric type effect in the region of highly dilute solution in order to ascertain the general character of the discrepancies from the simple Debye-Hückel theory and to correlate the empirical results so obtained with the validity of the fundamental physical assumptions of the theory.

THEORY OF EXPERIMENTAL METHOD.

Of the various methods such as Freezing Point Depression, Electro-Motive Force, Vapor Pressure Depression, etc., which may be used to evaluate the thermodynamic properties of ions, none give more accurate results in highly dilute solutions than the method of measuring the Activity Coefficient by the change in solubility of difficulty soluble solutes in the presence of solvent salts of changing concentration. The theory of this method has been treated in detail by a number of writers [(Lewis and Randall, Thermodynamics, Loc. Cit. p. 369) (et. seq. Eucken, Jette and La Mer, p. 322-3.)] It depends upon the fact that the activity of the dissolved molecules in equilibrium with a definite solid phase is a constant at constant temperature. Thus the activity is independent of the nature of the solvent, but the activity coefficient varies inversely as the

stoichiometric solubility. If we define S as the stoichiometric solubility in moles per liter, f as the activity coefficient, we have

$$A = f_0 S_0 = f_1 S_1 = f_2 S_2$$

where the subscript $_0$ refers to pure water as solvent and the subscripts 1, 2, etc., refer respectively to any solvent prepared by adding foreign substances to pure water, it follows that

$$-\text{Log } f_1 = \text{Log } \frac{S_1}{S_0} - \text{Log } f_0$$

The value of (—Log. f_0) was determined by plotting the experimental values of Log. $\frac{S_1}{S_0}$ as ordinates against the square root of the ionic strength as abscissae. It is clear from figures (II., III., and IV.) that these curves are rapidly approaching a straight line at a point on the abscissa which is equal to the $\sqrt{\mu}$ of the saturating salt in pure water. Owing to this linear character and the marked insolubility of the salts it is possible to evaluate —Log. f_0 very accurately by performing graphically the resulting short extrapolation from the ionic strength of a saturated solution of the difficultly soluble salt in pure water to infinite dilution. The ordinate where the Log $\frac{S_0}{S_1}$ line cuts the line of zero ionic strength gives the value of —Log. f_0.

The solubility effects of strong electrolytes upon very insoluble salts have been reviewed in the well known works of [Harkins, J. A. C. S., 191, (1916 to 1918), A. A. Noyes, J. A. C. S., 33, 1643 (1911), and Brönsted, J. A. C. S., 42, 760 (1921).] In the careful experiments reported by the latter author there can be found results of the effects of at least twelve electrolytes of different valence types upon a series of insoluble salts of (1—1) (2—1) (3—1) and (3—3) valence types. Moreover in the series of twelve electrolytes, various individual types of electrolytes were duplicated the object being to ascertain the specific effects of various anions and cations.

The need for further experimental work on this subject will be apparent when the data of Brönsted and Peterson are reconsidered in the light of the Debye theory by the use of Equations I and IVa as we have shown in Figures I, VII and IX. In the majority of cases their data is too meagre to determine the nature of the deviations from the Ideal Equation I. particularly in certain crucial ranges of concentration. Thus, if we examine the data of Brönsted and Peterson relating to the effect of $MgSO_4$ (see Figure I) on $Co(NH_3)_6$ $[(Co(NH_3)_2(NO_2)_4)]_3$ Luteo di-ammino Tera nitro Cobaltiate (3—1) type it is evident that there is an insufficient number of points to determine whether in highly dilute solution the $MgSO_4$ curve joins the ideal curve for point charges by passing through a point of inflection or not as indicated by the dotted portions a, and b. The importance of this point will be discussed later.

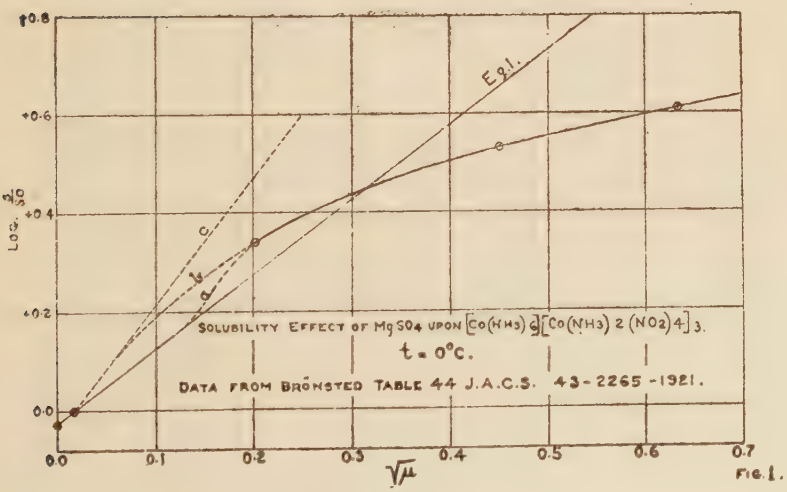

FIG. I.

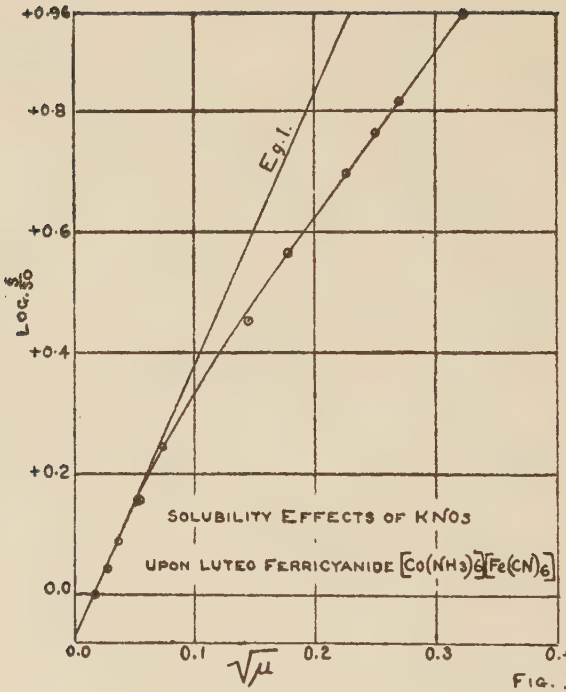

FIG. II

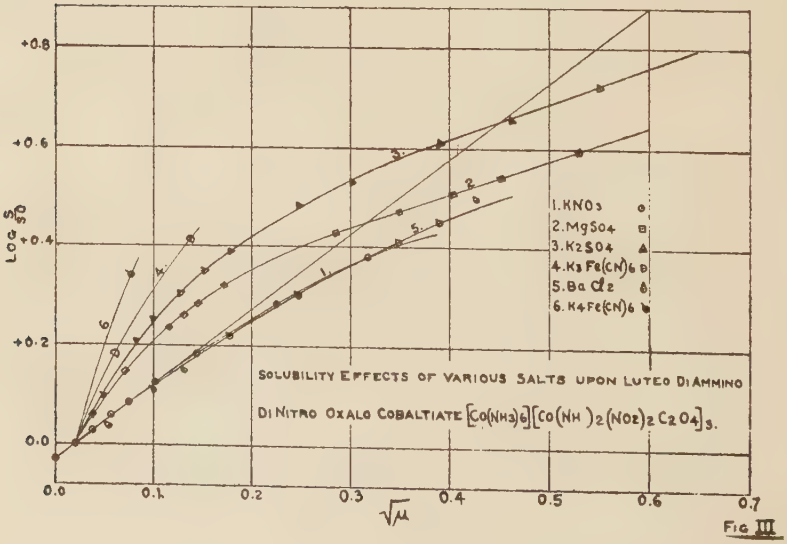

FIG III

TABLE I.

SOLUBILITY RELATIONS OF $Co[(NH_3)_6]\cdot[(Fe(CN)_6]$

Table 49—Brönsted, J. A. C. S., 43, 2265, 1921.

Solvent Moles per Liter	Solubility Moles per Liter	μ	$\sqrt{\mu}$	Log S/So	—Log f found	—Log f calc.	Diff.
			SOLVENT WATER				
	0.0000098	0.0000882	0.009392		0.0400	0.0426	
			SOLVENT KCl				
0.05	0.0000534	0.05048	0.2247	0.7363	0.7763	1.0212	—0.2449
0.10	0.0000911	0.1008	0.3175	0.9683	1.0083	1.4430	—0.4347
0.20	0.0001724	0.2015	0.4490	1.2453	1,2853	2.0407	—0.7554
0.50	0.0004620	0.5041	0.7100	1.6734	1.7134	3.2269	—1.5135
0.75	0.0007510	0.7567	0.8698	1.8844	1.9244	3.9532	—2.0288
1.00	0.0010790	1.0097	1.0040	2.0419	2.0819	4.5632	—2.4813
2.00	0.0027200	2.0244	1.4220	2.4434	2.4834	6.4629	—3.9795

TABLE II.

SOLUBILITY RELATIONS OF $Co(NH_3)_6\cdot[Co(NH_3)_2(NO_2)_4]_3$

Table 44—Brönsted, J. A. C. S., 43, 2265, 1921.

			SOLVENT WATER				
	0.000043	0.000258	0.01606		—0.0256	—0.02433	
			SOLVENT $MgSO_4$				
0.01	0.0000948	0.04056	0.2014	0.3433	0.3689	0.3051	+0.0638
0.05	0.0001440	0.2008	0.4481	0.5249	0.5505	0.6788	—0.1283
0.10	0.0001730	0.4010	0.6333	0.6045	0.6301	0.9594	—0.3293

SOLUBILITY RELATIONS OF $[Co(NH_3)_4C_2O_4]_3 \cdot [Cr_2(CNS)_6]$

Table 46—Brönsted, J. A. C. S., 43, 2265, 1921.

Solvent Moles per Liter	Solubility Moles per Liter	μ	$\sqrt{\mu}$	Log S/So	—Log f found	—Log f calc.	Diff.
			SOLVENT WATER				
	0.000532	0.003192	0.05650		0.08072		
			SOLVENT $MgSO_4$				
0.001	0.000586	0.007516	0.08668	0.0420	0.1227	0.1313	—0.0086
0.005	0.000687	0.02412	0.1553	0.1111	0.1918	0.2352	—0.0434
0.010	0.000766	0.04459	0.2112	0.1583	0.2390	0.3199	—0.0809
0.050	0.001100	0.2066	0.4545	0.3155	0.3962	0.6885	—0.2923

SOLUBILITY RELATIONS OF $[Co(NH_3)_4Cl_2]_3 \cdot [Fe(CN)_6]$

Table 47—Brönsted, J. A. C. S., 43, 2265, 1921.

			SOLVENT WATER				
	0.000121	0.000726	0.02694		0.0368		
			SOLVENT $MgSO_4$				
0.005	0.000149	0.020894	0.1445	0.9004	0.1272	0.2189	—0.0917
0.010	0.000167	0.041002	0.2025	0.1339	0.1767	0.3067	—0.1300
0.050	0.000222	0.201332	0.4487	0.2636	0.3004	0.6797	—0.3793
0.100	0.000251	0.401506	0.6336	0.3169	0.3537	0.9599	—0.6062

EXPERIMENTAL PART

Saturating salts suitable for our purpose must satisfy a number of criteria: (a) They must be sufficiently insoluble so that one can work in highly dilute solution. (b) On the other hand the salts must not be too insoluble or else it will be difficult to obtain an accurate determination of the solubility, salts containing a large number of ammonia groups are best suited for this purpose. (c) Ions of the solvent salts used must not form precipitates with the ions of the saturating salts used (d) saturating salts must be stable in aqueous solution at the temperature investigated and possess definite crystalline forms.

It is obvious that salts possessing all these qualifications are not easy to find. In this paper we will present experimental data on three cobalt-amines having solubilities in water ranging from 0.00003 to 0.0001 M. which fulfill these requirements satisfactorily. Their formulae and names have been mentioned in the Introduction and in Tables (III. to V.) where their complete solubility relations in various solvents are tabulated.

Preparation of Saturating Salts.

(Ref. Biltz Lab. Methods of Inorganic Chemistry p. 176). $[Co(NH_3)_6(NO_3)_3]$ 24 gr. Cobaltous carbonate were dissolved in concentrated nitric acid, (Sp. g. 1.38) filtered and diluted to double the original volume. A measured quantity (200 c.c.) of concentrated ammonium hydroxide (Sp. g. 0.88) was then added, the resulting solution was heated to boiling and the cobaltous ion was oxidized by adding 25.4 grams of resublimed iodine. A vigorous reaction took place and the resulting solution was allowed to stand for two hours until the precipitate had settled. The latter was removed by filtration, washed with water containing ammonia and then boiled with 200 c.c. of concentrated nitric acid whereby the iodine is recovered by condensation. The salt was washed with dilute nitric acid, then with alcohol and finally dried in the hot closet.

Preparation of $K \cdot [Co(NH_3)_2(NO_2)_4]$

(J.A.C.S. 38, 2647, (1916) Harkins, Hall & Roberts).

100 grams of cobaltous carbonate were converted into the chloride by means of dilute Hydrochloric acid, 200 grams of Ammonium Chloride crystals were added, and the resulting solution was maintained for half an hour at 50° C. A concentrated solution of Potassium nitrate containing 100 grams was then added with constant stirring. After approximately twenty minutes a fine yellow powder separated then later dark brown crystals. The latter were recovered by dissolving in hot water and filtering off the insoluble yellow powder. The dark brown crystals obtained from the filtrate were recrystallized from distilled water.

Note. The insoluble yellow powder was $K_3Co(NO_2)_6$.

Preparation of $(Co(NH_3)_2(NO_2)_2C_2O_4)\cdot K.H_2O$
(Jorgensen, Z. Anorg. Chemie, 11, 248 (1896).)

10 grams of Crystallized oxalic acid were dissolved in 50 c.c. of water and this solution was added to 100 c.c. of a solution containing 20 grams of $(Co(NH_3)_2(NO_2)_4).K$. After being heated to about 50° C. evolution of NO_2 followed with separation of a precipitate. The latter was removed by filtration and washed with cold water. It was purified by recrystallization from hot water.

$(Co(NH_3)_2(NO_2)_2C_2O_4)_3\cdot(Co(NH_3)_6)\cdot 6H_2O$
(Jorgensen, Z. Anorg. Chemie, 5, 179 (1894).)

This salt was quantitatively precipitated from an aqueous solution of 160 liters volume by allowing a saturated solution of $(Co(NH_3)_6)$, $(NO_{33}$ and $(Co(NH_3)_2(NO_2)_2C_2O_4)$. K. H_2O to drip simultaneously into 16 liters of distilled water, which was thoroughly agitated by an electric stirrer while the supernatant liquid was syphoned off and replaced by fresh water ten times during the course of preparation. This procedure facilitated the growth of well-defined crystals, which were necessary for subsequent operations in the investigation.

Analysis per cent. Co., 22.62 Theoretical 22.76.

Ref. Jorgensen, Z. Anorg. Chemie, 11, 440 (1894); 5, 179, (1894). $Co(NH_3)_6)$, $(Co(NH_3)_2\ (NO_2)_4)_3$.

This salt was quantitatively precipitated from an aqueous solution by adding simultaneously $(Co(NH_3)_6)$, $(NO_3)_3$ and $(Co\ (NH_3)_2\ (NO_2)_4)$. K in equivalent quantities to 160 liters of distilled water under conditions identical with those described above.

The reason for precipitating the final products from highly dilute solutions is to minimize the chance of the precipitate carrying down traces of foreign salts, which are difficult to remove by washing if they become mixed in the crystal lattice.

This compound was analyzed by decomposing a weighed quantity with sulphuric acid evaporating to constant weight and weighing the cobalt as cobaltous sulphate. The average of two determinations showed 23.40 per cent. cobalt while the theoretical is 23.78 per cent.

The preparation of the saturated solutions was carried out in a large specially constructed Freas Thermostat maintained at 25°. As the solubilities of the cobalt ammine salts used as saturating salts in this investigation increase on an average about 5-10 per cent., per degree it was necessary to maintain the temperature constant to 0.01°. No fluctuations greater than 0.005° were ever observed with thermometers kept constantly near two opposite corners of the bath.

Four two-liter glass bulbs (Fig. I) (Brönsted and Le Mer J. A. C. S., 46, 555, 24) similar to those shown were employed to hold the solvent liquid which flowed slowly through a layer of the solute contained in the tube leading from the bulb. A plug of cotton served as a support and filter for the solute salt. A salt column 20 cm. long allowed about 500 c.c. of liquid to pass through into the collecting flask in 24 hours.

Experiments in which the rate of flow of the solvent through the sat. salt was varied showed that this factor had no influence upon our results, which we take as evidence of saturation.

The method of obtaining the saturated solutions by use of the apparatus described above is much superior for the present purposes to the methods usually employed as it enables one to carry out a complete series of experiments

using different concentrations of salt solution as solvents and a single sample of saturating salt, thereby eliminating any chance of error due to differences in the physical properties of the saturating salt. A second sample of saturating salt was not used throughout the investigation. Moreover to obtain crystals of uniform size these saturating salts were shaken for a period of two weeks and the wash water was changed every twelve hours to remove impurities carried mechanically upon the exterior surface of the crystals.

At intervals of six weeks the saturating salts were thoroughly drained of any solvent salt, then thoroughly washed and a new value of its solubility in water was obtained. No differences outside the experimental error were ever observed.

The analyses were performed by measuring a fixed quantity of the saturated solution—250 c.c. for determinations where the concentration of solvent salt was less than 0.01 M and 100 c.c. where the concentration of solvent salt was greater than 0.01 M—adding sufficient Sodium Hydroxide to make the final mixture about 0.1 M in alkali and distilling the ammonia, which is liberated on boiling into a known quantity of 0.01076 N. Hydrochloric acid through a block tin condenser tube. Methyl red was used as indicator in making the titrations.

Owing to the large number of equivalents of ammonia liberated per mole of cobalt ammine it was possible by averaging the results of four or more distillations to attain an accuracy of one or at most two parts per thousand in the determination of the ammonia liberated except in the case of the very insoluble luteo ferricyanide where we claim an accuracy of four parts per thousand.

Preliminary experiments were performed for the purposes of investigating the best conditions under which to decompose the salt so that the loss of ammonia in bubbling through the standard acid would be a minimum.

In Figures V. and VI. we have plotted the number of cubic centimeters of acid added as ordinates against time in minutes from the moment a very small flame was applied.

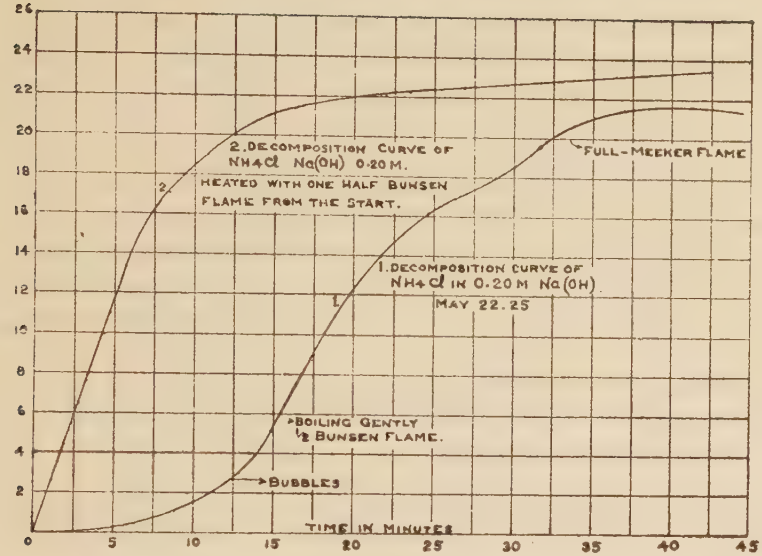
2. DECOMPOSITION CURVE OF NH4Cl Na(OH) 0·20 M.
HEATED WITH ONE HALF BUNSEN FLAME FROM THE START.
FULL-MEEKER FLAME
1. DECOMPOSITION CURVE OF NH4Cl IN 0·20 M Na(OH) MAY 22.25
BOILING GENTLY ½ BUNSEN FLAME.
BUBBLES
TIME IN MINUTES

FIG. V

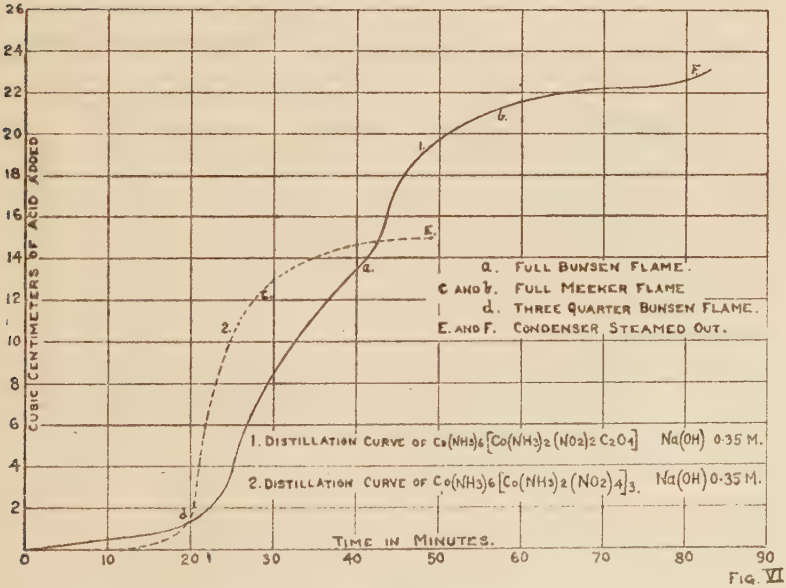
CUBIC CENTIMETERS OF ACID ADDED
a. FULL BUNSEN FLAME.
c AND b. FULL MEEKER FLAME
d. THREE QUARTER BUNSEN FLAME.
E. AND F. CONDENSER STEAMED OUT.
1. DISTILLATION CURVE OF Co(NH3)6[Co(NH3)2(NO2)2C2O4] Na(OH) 0·35 M.
2. DISTILLATION CURVE OF Co(NH3)6[Co(NH3)2(NO2)4]3. Na(OH) 0·35 M.
TIME IN MINUTES.

FIG. VI

The ammonia evolved was absorbed in 50 cubic centimeters of distilled water to which three drops of methyl red had been added and acid was added in one cubic centimeter portions every time the indicator showed an alkaline reaction. The number of cubic centimeters of acid represented on the ordinate is a measure of the ammonia evolved. Moreover from inspection of these curves it is obvious that the best procedure was to heat with a very small flame for fifty minutes, until the solution in the generating flask was boiling gently, then substitute a meeker burner and boil vigorously until the reaction mixture had been evaporated almost to dryness. During the latter operation the condenser was steamed out by checking the flow of cooling water and turning the same on again when steam was being evolved vigorously through the standard acid in the absorption flask. Blank determinations of ammonia were run on the water and reagents and these constant corrections are taken care of along with the corrections due to burettes in the data (sheet) under heading marked ("Corrected Volume of acid.")

To avoid any errors from carbon dioxide due to its effect upon the indicator methyl red, distilled water, which had been redistilled over acid potassium permanganate was used in all operations throughout the investigation; and in using the water soda lime guards were used on the reagent and wash bottles.

To facilitate a uniform end point in all titrations a standard buffer solution was made up of acetic acid and sodium acetate to which three drops of methyl red had been added and all end points were matched with this standard. The concentration of this buffer solution was such that the degree of acidity was pH 5. C. P. chemicals were used throughout the investigation and those used for solvent salts were recrystallized thrice from conductivity water and carefully dried before making up to the volume concentration desired.

TABLE III.

SOLUBILITY RELATIONS OF $[Co(NH_3)_6]\cdot[Fe(CN)_6]$

No. of Sol. Tube	Conc. Solvent M/L	C. C. Acid	C. C. Acid corr.	Solubility Moles per Liter	μ	$\sqrt{\mu}$	Log S/So	Log S/So —Log f_o. —Log f found	—Log f —Log f calc. $= \alpha Z.Z_2\sqrt{\mu}$	Diff.
					SOLVENT WATER					
II., IV.	....	4.51	4.08	0.00002925	0.0002632	0.01622	....	0.07681	0.07371	
					SOLVENT KNO_3					
	0.0005	5.06	4.53	0.00003248	0.0007923	0.02815	0.0455	0.1223	0.1280	—0.0057
	0.0010	5.54	5.07	0.00003635	0.001327	0.03643	0.0944	0.1712	0.1656	+0.0056
	0.0030	6.57	6.03	0.00004323	0.003389	0.05820	0.1697	0.2465	0.2645	—0.0180
	0.0050	7.87	7.47	0.00005356	0.005482	0.07404	0.2627	0.3395	0.3365	+0.0030
	0.0100	9.60	9.20	0.00006596	0.01059	0.1030	0.3532	0.4300	0.4681	—0.0381
	0.0200	12.80	12.39	0.00008883	0.02080	0.1443	0.4824	0.5592	0.6558	—0.0966
	0.0300	16.63	16.19	0.00011608	0.03104	0.1762	0.5986	0.6754	0.8008	—0.1254
	0.0500	22.39	22.00	0.0001577	0.05142	0.2268	0.7317	0.8085	1.0308	—0.2223
	0.0600	26.75	25.76	0.0001847	0.06166	0.2483	0.8003	0.8771	1.1285	—0.2514
	0.7000	29.62	29.26	0.0002098	0.07189	0.2681	0.8557	0.9325	1.2185	—0.2860
	0.1000	40.61	40.26	0.0002886	0.1026	0.3203	0.9942	1.0710	1.4558	—0.3847

TABLE IV.

SOLUBILITY RELATIONS OF $[Co(NH_3)_6] \cdot [Co(NH_3)_2(NO_2)_2C_2O_4]$

No. of Sol. Tube	Conc. Solvent M/L	C. C. Acid	C. C. Acid corr.	Solubility Moles per Liter	μ	$\sqrt{\mu}$	Log S/So	Log S/So —Log f_o. —Log f found	—Log f —Log f calc. $= \alpha Z.Z_2\sqrt{\mu}$	Diff.
					SOLVENT WATER					
I., II., III.	0.0000	23.02	22.60	0.00008104	0.0004862	0.02205	....	0.0336	0.03340	
					SOLVENT KNO_3					
I., II., III.	0.001	24.33	23.99	0.00008603	0.001516	0.03894	0.0260	0.0596	0.05900	+0.0006
	0.005	28.14	27.71	0.00009937	0.005596	0.05966	0.0605	0.0941	0.09038	+0.0038
	0.010	30.60	30.17	0.0001082	0.01065	0.07480	0.0885	0.1221	0.1133	+0.0088
	0.020	34.93	34.50	0.0001237	0.02074	0.1032	0.1255	0.1591	0.1563	+0.0028
	0.050	44.00	43.59	0.0001563	0.05094	0.1440	0.1836	0.2172	0.2182	—0.0010
	0.100	55.62	55.29	0.0001982	0.1012	0.2257	0.2852	0.3188	0.3420	—0.0232
	0.003	26.37	25.98	0.00009316	0.003560	0.3181	0.3884	0.4220	0.4819	—0.0599
					SOLVENT SALT K_2SO_4					
I., II., III.	0.0005	28.88	28.45	0.0001020	0.002112	0.04595	0.0999	0.1335	0.06961	+0.0689
	0.0010	32.58	32.17	0.0001153	0.003692	0.06076	0.1531	0.1867	0.09205	+0.0947
	0.0030	41.39	40.94	0.0001468	0.009881	0.09940	0.2581	0.2917	0.1506	+0.1411
	0.0050	46.79	46.28	0.0001660	0.01600	0.1265	0.3114	0.3450	0.1916	+0.1534
	0.0070	51.03	50.51	0.0001811	0.02209	0.1486	0.3492	0.3828	0.2251	+0.1577
	0.0100	57.35	56.26	0.0002017	0.03121	0.1767	0.3960	0.4296	0.2677	+0.1619
	0.0200	69.92	69.59	0.0002495	0.06150	0.2480	0.4884	0.5220	0.3757	+0.1465
	0.0300	77.80	77.71	0.0002787	0.09170	0.3028	0.5364	0.5700	0.4587	+0.1113
	0.0500	83.57	93.31	0.0003346	0.1520	0.3899	0.6158	0.6494	0.5907	+0.0587
	0.0700	106.27	105.76	0.0003792	0.2123	0.4607	0.6701	0.7037	0.6979	+0.0058
	0.1000	121.97	121.41	0.0004354	0.3026	0.5500	0.7303	0.7639	0.8332	—0.0693

No. of Sol. Tube	Conc. Solvent M/L	C. C. Acid	C. C. Acid corr.	Solubility Moles per Liter	μ	$\sqrt{\mu}$	Log S/So	Log S/So $-\log fo.$ $-\log f$ found	$-\log f$ $-\log f$ calc. $= aZ.Z_2\sqrt{\mu}$	Diff.
				SOLVENT SALT $K_3Fe(CN)_6$						
I., II., III.	0.0005	34.62	34.22	0.0001227	0.003736	0.06112	0.1801	0.2137	0.09259	+0.1211
	0.0010	35.90	35.53	0.0001274	0.006764	0.08224	0.1965	0.2301	0.1246	+0.1055
	0.0030	59.07	58.71	0.0002105	0.019260	0.1388	0.4145	0.4481	0.2103	+0.2378
				SOLVENT SALT $K_4Fe(CN)_6$						
I., II., III.	0.0005	49.94	49.55	0.0001777	0.006066	0.07788	0.3410	0.3746	0.1180	+0.2566
				SOLVENT SALT $MgSO_4$						
I., II., III.	0.0002	26.28	25.79	0.00009248	0.001355	0.03681	0.0574	0.0910	0.05576	+0.0352
	0.0005	28.71	28.28	0.0001014	0.002608	0.05107	0.0973	0.1309	0.07737	+0.0535
	0.0010	31.95	31.45	0.0001128	0.004677	0.06839	0.1435	0.1771	0.1036	+0.0735
	0.0030	40.06	39.59	0.0001420	0.01285	0.1134	0.2436	0.2772	0.1718	+0.1054
	0.0040	42.13	41.60	0.0001492	0.01689	0.1300	0.2651	0.2987	0.1969	+0.1018
	0.0050	44.68	44.18	0.0001584	0.02095	0.1447	0.2911	0.3247	0.2192	+0.1055
	0.0070	47.88	47.38	0.0001699	0.02902	0.1703	0.3216	0.3552	0.2580	+0.0972
	0.0200	62.27	61.69	0.0002212	0.08133	0.2852	0.4361	0.4697	0.4321	+0.0376
	0.0300	67.97	67.56	0.0002423	0.1214	0.3484	0.4756	0.5092	0.5278	—0.0186
	0.0400	74.47	73.91	0.0002650	0.1616	0.4020	0.5145	0.5481	0.6090	—0.0609
	0.0500	79.47	78.96	0.0002831	0.2017	0.4491	0.5433	0.5769	0.6804	—0.1035
	0.0700	90.30	89.84	0.0003222	0.2819	0.5309	0.5995	0.6331	0.8043	—0.1712

No. of Sol. Tube	Conc. Solvent M/L	C. C. Acid	C. C. Acid corr.	Solubility Moles per Liter	μ	$\sqrt{\mu}$	Log S/So	Log S/So —Log *fo*. —Log *f* found	—Log *f* —Log *f* calc. $= \alpha Z.Z_2\sqrt{\mu}$	Diff.
				SOLVENT SALT $BaCl_2$						
I., II., III.	0.0005	25.01	24.52	0.00008793	0.002028	0.04504	0.0354	0.0690	0.06823	+0.00077
	0.0010	26.18	25.79	0.00009248	0.003555	0.05962	0.0574	0.0910	0.09032	+0.0007
	0.0030	29.73	29.30	0.0001051	0.009630	0.09813	0.1129	0.1465	0.1486	—0.0021
	0.0050	32.49	32.02	0.0001148	0.01569	0.1253	0.1512	0.1848	0.1898	—0.0048
	0.0100	37.99	37.52	0.0001345	0.03081	0.1755	0.2200	0.2536	0.2659	—0.0123
	0.0200	45.88	45.42	0.0001629	0.06098	0.2469	0.3032	0.3368	0.3740	—0.0372
	0.0400	58.80	58.34	0.002092	0.1212	0.3481	0.4118	0.4454	0.5274	—0.0820
	0.0500	64.32	64.91	0.0002327	0.1514	0.3889	0.4581	0.4917	0.5892	—0.0975
	0.0600	72.62	72.19	0.0002588	0.1815	0.4260	0.5043	0.5379	0.6454	—0.1075

TABLE V.

SOLUBILITY RELATIONS OF $[Co(NH_3)_6]\cdot[Co(NH_3)_2(NO_2)_4]_3$

				SOLVENT WATER						
IV.	....	11.98	11.80	0.0001634	0.0009804	0.03131	....	0.0464	0.4743	
				SOLVENT SALT K_2SO_4						
IV.	0.0010	16.65	16.50	0.0002285	0.004371	0.06611	0.1456	0.1920	0.1001	+0.0919
	0.0050	23.65	23.50	0.0003255	0.01695	0.1302	0.2993	0.3457	0.1972	+0.1485
	0.0100	28.38	28.20	0.0003906	0.03234	0.1798	0.3785	0.4249	0.2724	+0.1525
	0.0500	46.40	46.11	0.0006386	0.15383	0.3921	0.5919	0.6383	0.5940	+0.0442
	0.1000	60.03	59.95	0.0008303	0.30498	0.5523	0.7059	0.7523	0.8367	—0.0844

No. of Sol. Tube	Conc. Solvent M/L	C. C. Acid	C. C. Acid corr.	Solubility Moles per Liter	μ	$\sqrt{\mu}$	Log S/So	Log S/So $-\log fo.$ $-\log f$ found	$-\log f$ $-\log f$ calc. $= \alpha Z.Z_2\sqrt{\mu}$	Diff.
					SOLVENT SALT $MgSO_4$					
I.	0.0010	16.04	15.90	0.0002202	0.005321	0.07293	0.1296	0.1760	0.1105	+0.0655
	0.0050	22.30	22.14	0.0003066	0.02184	0.1478	0.2733	0.3197	0.2239	+0.0958
	0.0100	25.69	25.56	0.0003540	0.04212	0.2053	0.3357	0.3821	0.3110	+0.0711
	0.0500	39.35	39.20	0.0005430	0.20326	0.4509	0.5215	0.5679	0.6831	—0.1152
					SOLVENT SALT KNO_3					
I.	0.0010	12.44	12.29	0.0001702	0.0020212	0.04496	0.0177	0.0641	0.06811	—0.00401
	0.0050	14.34	14.15	0.0001960	0.006176	0.07859	0.0790	0.1254	0.1190	+0.0064
	0.0500	21.98	21.83	0.0003023	0.051814	0.2276	0.2672	0.3136	0.3448	—0.0312
	0.1000	26.98	26.86	0.0003720	0.102232	0.3197	0.3573	0.4037	0.4843	—0.0806
					SOLVENT SALT $NaNO_3$					
I.	0.0010	12.49	12.33	0.0001708	0.002025	0.04501	0.0192	0.0656	0.06819	—0.0026
	0.0050	14.08	13.93	0.0001930	0.006158	0.07848	0.0723	0.1187	0.1189	—0.0002
					SOLVENT SALT $BaCl_2$					
I.	0.0010	13.33	13.04	0.0001806	0.004084	0.06390	0.0434	0.0898	0.09681	—0.0070
	0.0030	14.77	14.67	0.0002032	0.01022	0.1011	0.0947	0.1411	0.1532	—0.0121
	0.0100	18.13	17.98	0.0002490	0.31495	0.1774	0.1829	0.2293	0.2688	—0.0395
	0.0200	20.92	20.77	0.0002876	0.061726	0.2484	0.2455	0.2919	0.3763	—0.0844
	0.0300	23.40	23.11	0.0003201	0.091920	0.3032	0.2920	0.3384	0.4593	—0.1209
	0.0500	26.88	26.70	0.0003698	0.152219	0.3901	0.3547	0.4011	0.5910	—0.1899
	0.1000	33.63	33.48	0.0004637	0.302782	0.5503	0.4529	0.4993	0.8337	—0.3344

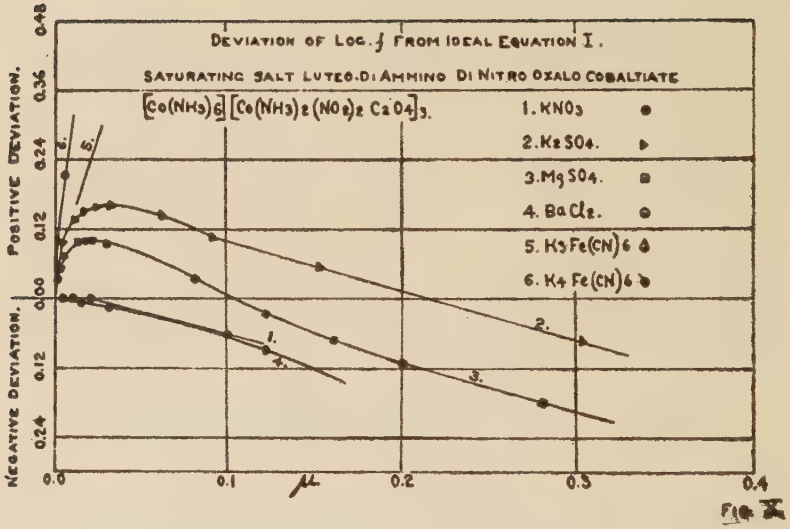
Deviation of Log. f from Ideal Equation I.
Saturating Salt Luteo-Di Ammino Di Nitro Oxalo Cobaltiate
[Co(NH3)6][Co(NH3)2(NO2)2 C2O4]3.
1. KNO3
2. K2SO4.
3. MgSO4.
4. BaCl2.
5. K3Fe(CN)6
6. K4Fe(CN)6
Positive Deviation.
Negative Deviation.
0.48
0.36
0.24
0.12
0.00
0.0
0.1
0.2
0.3
0.4
μ

Fig X

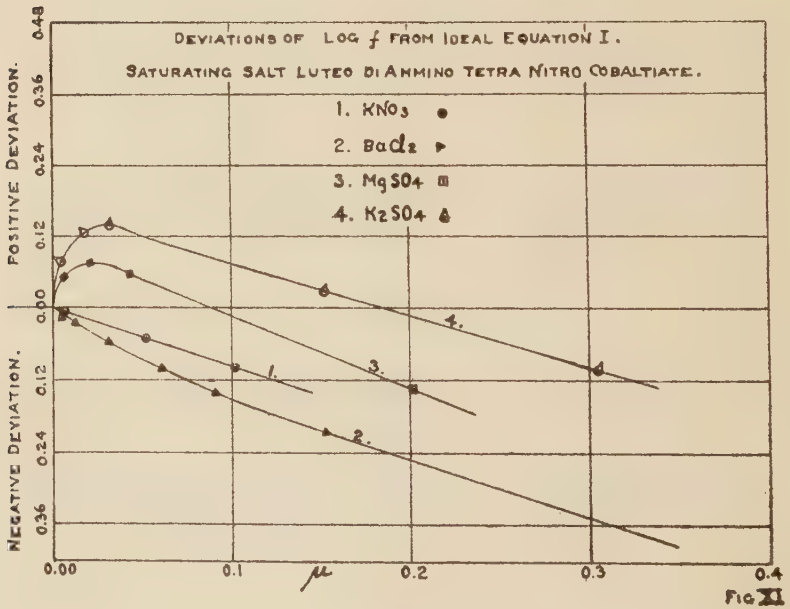
Deviations of Log f from Ideal Equation I.
Saturating Salt Luteo Di Ammino Tetra Nitro Cobaltiate.
1. KNO3
2. BaCl2
3. MgSO4
4. K2SO4
Positive Deviation.
Negative Deviation.
0.48
0.36
0.24
0.12
0.00
0.00
0.1
0.2
0.3
0.4
μ

Fig XI

DISCUSSION OF RESULTS

The results of this investigation may be presented most clearly by plotting the deviations, which the experimental data exhibit, from the law of ideal salt solutions represented by Equation I., as a function of the first power of the "ionic strength." If equations (III and III-A) are correct representations of the facts then in dilute solutions we should obtain at low concentrations a linear negative deviation as expressed by Equation III-A followed by a less rapid decrease at higher concentrations due to the influence of higher terms. In view of the fact that we shall always subtract from the experimental values the values, calculated by Equation I., it is highly important to be certain that the numerical value of α^1 as predicted theoretically by the Debye-Hückel theory and as tested experimentally by Brönsted and La Mer is correct, since the calculated deviations from Equation I will be sensitive to changes in the value of α^1.

We have chosen the tri-trivalent salt Luteo Ferricyanide $(Co(NH_3)_6)\cdot(Fe(CN)_6)$ to redetermine α^1. Owing to the high valence product of this Salt $(-3.-3) = +9$ it is possible to evaluate α^1 with nine times the accuracy which one could obtain with a uni univalent saturating salt, provided that other factors such as experimental accuracy in solubility determinations remain equal. Moreover its solubility (0.00003 Molar at 25°) is such that only a very short extrapolation is necessary to evaluate $-\text{Log}_{10} f_0$. Most important of all, since the valences of the cation and anion of Luteo ferricyanide are equal, this salt should be free from any disturbing influences due to inequality in the valences, when it is dissolved in a solvent salt like Potassium Chloride or Potassium Nitrate; i.e., $\sum_1^5 njZj^3$ will always equal zero. The data of Table III when plotted as in Figure II show that the experimental curve rapidly approaches and merges into the ideal curve of Equation I when α^1 is given the theoretical value (0.505 at 25° C.). We have accordingly used this theoretical value of α^1 through-

out all of the present work, and it is represented by the straight lines in Figures I, III, and IV.

The curves, showing the deviations from Equation I for Luteo Ferricyanide ($Co(NH_3)_6$), ($Fe(CH)_6$) are always negative in slope as demanded by Equation IIIa (see Figure VIII).

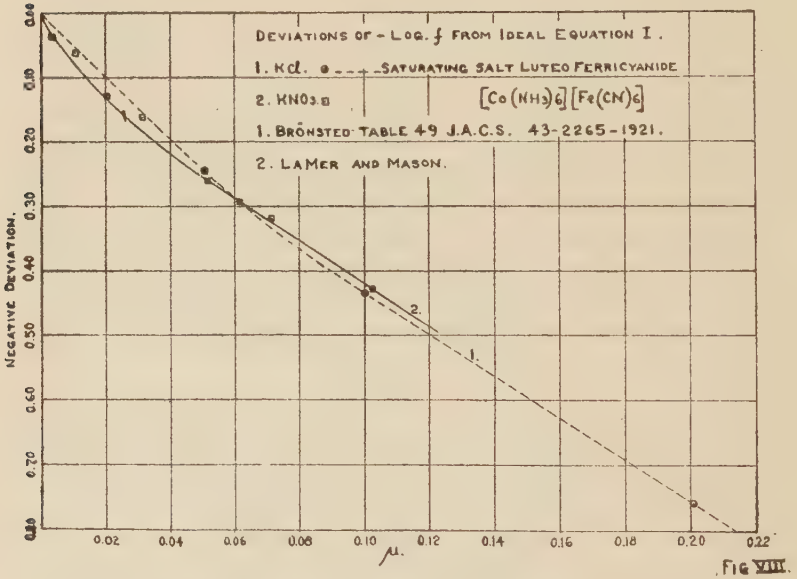

Fig VIII.

Therefore it would appear from the present data, that the assumptions made originally by Debye and Hückel in deriving Equation III, are correct in the main essentials, at least for the mixtures of symmetrical types of salts, as was shown previously by Schärer and others.

When we consider saturating salts possessing cations and anions of unequal valence (see Figures III and IV); namely, Lutea di-ammino di nitro oxale Cobaltiate a (3—1) type (So(25° C.) = 0.00008104 Molar) or Luteo di-ammino tetra nitro cobaltiate (So(25° C.) = 0.0001634 Molar), we find again that when the symmetrical solvent salts potassium nitrate or Sodium Nitrate are used, that the experimental curves behave very similarly to those shown for KNO_3 on Luteo Ferricyanide. When the valence type of the solvent salt is unsymmetrical

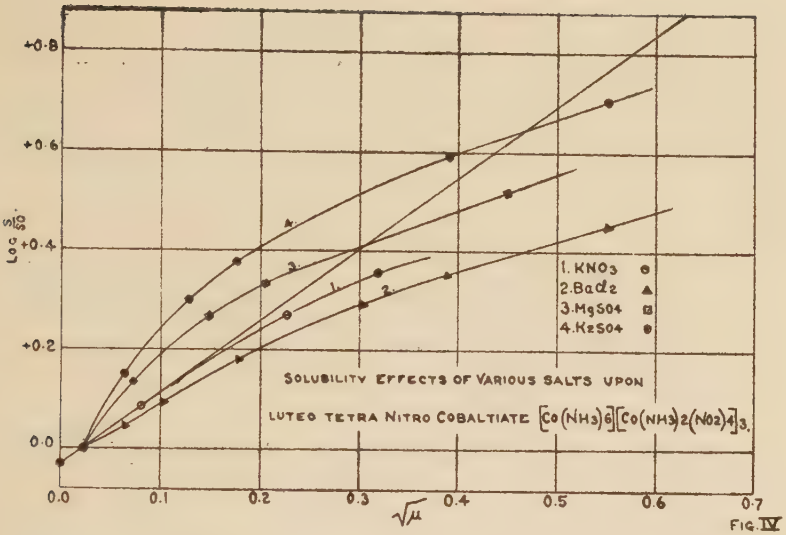

FIG. IV

but of the same sequence of inequality as in the case of Barium Chloride (2—1) the curves are again of the general shape demanded by Equations IIIa and IIIb. In fact a value of "a" = 1.53 10^{-8} fits the experimental data for $BaCl_2$ solutions remarkably well.

However, when we consider the data for solvent salts where the anion possesses a valence higher than unity; namely, Magnesium Sulphate (2—2) and Potassium Sulphate (1—2), we encounter the peculiarities first noted by Brönsted and Peterson. If their results and those of this paper are considered in the light of Equations I and III (shown in Figures VII and IX) it is plainly evident that *it would require negative values of "a" in the range of highly dilute solutions, followed by positive values in less dilute solutions (i.e. above* 0.17μ) *to account for the data.* Evidently some phenomena, which leads to larger solubilities, and which it not adequately represented by the Debye-Hückel theory in its present form, is manifesting itself. Further, the complication appears to be one which is most effective or predominant in highly dilute solution (a range of concentration varying from 0.001μ to 0.02μ) where the individual peculiarities of the ions ordinarily

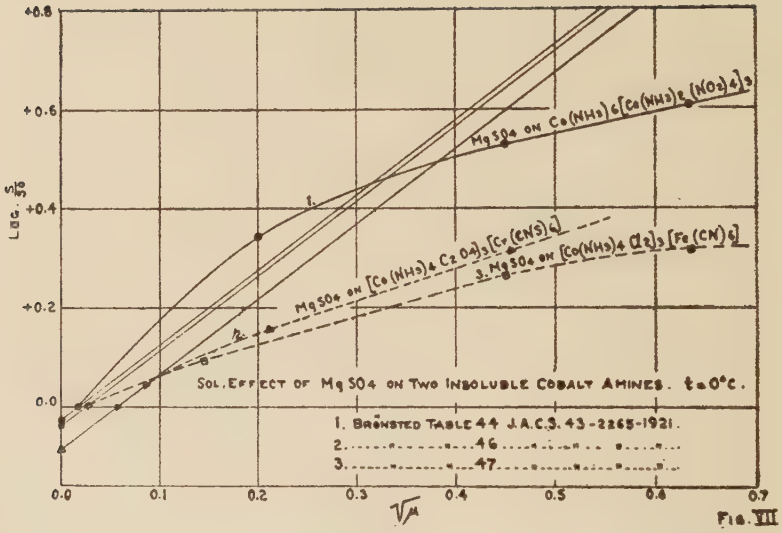

Fig. VIII

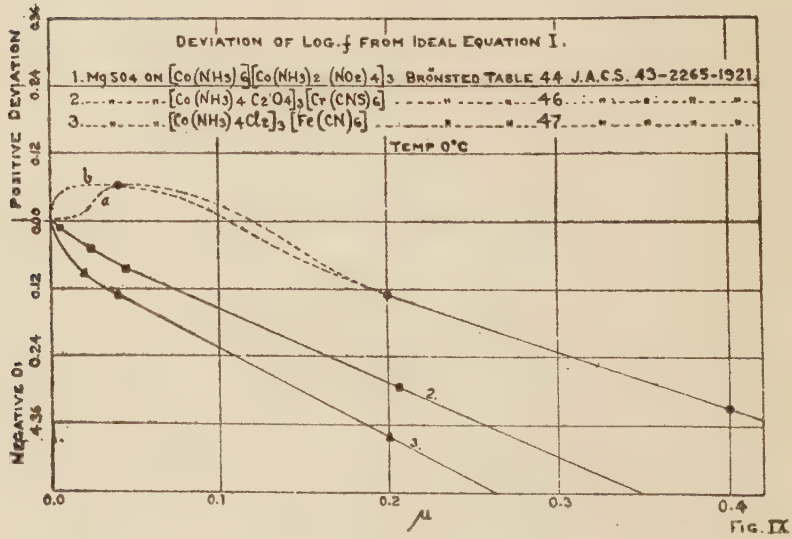

Fig. IX

vanish. As we pass to slightly more concentrated solutions (Ex. from 0.02μ to the highest concentration studied 0.30μ) we observe that the disturbing effect in the highly dilute range either vanishes or becomes completely obscured by an almost linear deviation which is negative in slope as predicted by Equation IIIa.

The question arises, what is the cause of the disturbing factor which appears to raise the normal deviation curves in a positive direction in highly dilute solution. As might be inferred from what precedes, the view was held throughout most of the period of this investigation, that it is due to the higher terms in the expansion of Equation V involving odd powers of the valence. Some preliminary calculations designed to test the influence of the higher terms of Equation V were made by the writer, but as stated previously proved to be too great a task to complete at this time. They are now being prosecuted in extenso by Professor La Mer and Dr. T. H. Grunwall. Their work however shows that although it is possible to obtain the unusual deviations of the same sign as those encountered with Potassium Sulfate by using positive values of "a" in the higher terms of Equation IIIb, yet the general forms of the curves so obtained and the exceptionally small values of "a" (usually less than $1.5\ 10^{-8}$) which are necessary to produce them make it unlikely that this can be the entire explanation of the phenomena, at least when the variation of the dielectric constant with concentration is neglected.

Without involving the aid of the complicated mathematical equations resulting from the expansion of Equation V it can be shown that some other factor of a physical nature not considered in the present form of the Debye theory must also be causing the phenomena observed with Potassium Sulphate and Magnesium Sulphate. For example the expansion of Equation V yields terms for the potential of an ion which increase in integer powers of the valence Z. Now all terms vanish at zero concentration and it is obvious that as the solution is made more dilute, that the influence of the higher terms must progressively vanish with dilution, with the result that the

experimental curve should fuse into and become identical with that of Equation I involving only the leading term; namely, the one involving the squares of the valences.

In other words the tangent of the experimental curve should uniformly approach and finally become identical with the tangent of Equation I. This behavior is represented by the dotted curve marked a in Figures I and IX.

The new experimental data obtained for $MgSO_4$ show quite conclusively that the actual behavior at the highest dilutions with which we have been able to work; namely (down to 0.00008 Molar) is like that represented by the curves b in Figures I and IX. In other words the tangent of the experimental curve at 0.00008 M. is not the same as that of Equation I.

We would expect even greater positive deviations with solvent salts like potassium ferrocyanide (1, —4 type) and potassium ferricyanide (1, —3 type) and this proves to be true. Unfortunately, the experiments with these solvent salts could not be extended beyond 0.003 Molar for potassium ferricyanide or 0.0005 Molar ferrocyanide, owing to the fact that a chemical re-arrangement occurred between the solute and solvent salts. Luteo ferricyanide and Luteo ferrocyanide were observed to precipitate at higher concentrations on several days standing. In fact the solubility values which are given for these two solvent salts may be somewhat in error for this reason.

In the case of potassium sulfate, we can definitely eliminate the possibility that the high solubility results might be due to an unobserved precipitation of Luteo Sulphate $(Co(NH_3)_6)_2(SO_4)_3$ because this latter salt possesses a solubility of 0.02 Molar (KS.P. $= 3.5\ 10^{-7}$) at 25° C. which would require a sulphate concentration of over two molar in order to produce precipitation. On the other hand, this calculation does not in itself eliminate the possibility that Luteo Sulphate might be a weak electrolyte and that the anamolous results may be due to incomplete dissociation.

Foot-note. The course of the dotted curves is somewhat exaggerated to show the different courses more clearly.

Furthermore, it seems highly improbable that the abnormal increase in solubility caused by the sulfates could be due to complex ion formation such as we have in the case of AgCl in the presence of excess (Ref. Kendall and Sloan, J. A. C. S., 47, 2306 (1925),) metal chlorides, for according to Werner's theory the co-ordination numbers of the complex cobalt ammines are satisfied, i.e., the residual valences of the cobalt ion are saturated. In view of the well known stability of the Luteo ion, it is likewise difficult to attempt to explain the results on the basis of a chemical substitution within the complex, say of the NH_3 groups by SO_4. If this should occur one would expect progressive changes in solubility, whereas we find that a definite solubility value can be promptly established and reproduced for each salt concentration used.

It seems that the most plausible explanation of the phenomena will be found by extending the first approximation in the Debye theory that ions may be considered as spheres to the more general assumption that certain ions, particularly the complex types, may possess a spheroidal or egg shaped form and that the electric charges within the molecule are not uniformly distributed, but are concentrated to a greater or less extent at the poles. Every non-spherical ion would accordingly have an electric moment which would be a specific individual constant for that ion depending upon the distribution of the charges. We suggest that this may be the explanation of Brönsted's specific interaction of ions of opposite sign, but until it has been possible to work out and verify the mathematical equations designed to account for the behavior under such an assumption, it does not seem advisable to speculate upon the validity of such a theory at the present time.

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